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Photoaction in the Course of Chelate Formation. II. Acidity and External Heavy-Atom Effects in the Boric Acid–Benzoylacetone Excited State Interaction

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The influence of acidity and of spin–orbital coupling (SOC) enhancement on benzoylacetone's (BZA) lowest excited-state interactions with proton and boric acid species is investigated. It is shown that S_1 state protolysis of BZA's conjugate chelate form (R) quenches the S_1 (R) $\rightsquigarrow$ T(R) process, thus lowering the triplet quantum yield of the ligand interacting with boron species and giving most probably a triplet non-chelate boron intermediate[1]*. SOC enhancements by external perturbations are found to increase the S ↔ T transition probabilities of all possible forms of BZA present in the solvents used. It is shown that manifestations, on lowest excited-state interactions of BZA, resulting from external heavy-atom effects on BZA photophysical processes, can be theoretically predicted and quantitatively checked. As in the case of solvated proton effects, results from heavy-atom effects are shown to be also consistent with boron species complexation by* ^{3}*BZA.*

Introduction

In part I of this work[1], the effect of irradiating benzoylacetone (BZA) at its 310 nm ICT band during the formation of the 1/1 borobenzoylacetonide chelate was investigated. It could be shown that excited-state contribution to complex formation takes place and that the BZA's photoreactive form is a T_1 protolysed hydrogen bonded structure (^{3}RH), interacting with boron species to give a triplet non-chelate boron intermediate. Evidence was brought that BZA's conjugate chelate form (R) also suffers protolysis in the S_1 state, so that one would expect proton concentration effects to be manifested on the rates of photoexcited pathways.

On the other hand, it was found that population of BZA's T_1 state in the form of ^{3}RH is mainly accomplished by the $^1R \rightsquigarrow {}^3R$ crossing, followed by proton disruption of the hydrogen bonded cycle. Therefore, enhancing spin–orbital coupling (SOC) in the ligand by an external heavy-atom perturbation should also affect the rates of photoexcited paths since, obviously, yields of ^{3}R and ^{3}RH formations and degradations have to be modified in the presence of perturber.

In the present work results from investigations of such effects (proton concentration and external heavy-atom perturbation) on the kinetics of the 1/1 boronbenzoylacetonide chelate formation in conc. H_2SO_4–ether irradiated solutions are reported and discussed.

Experimental

Reagents were purified and solutions prepared as described in part I of this work[1]. Ethyl iodide, chosen as heavy atom molecule, was of *puriss.* quality (Fluka) and used without further purification.

Irradiations of non-deaerated solutions were performed under the same conditions as previously[1], in an apparatus assembly described in part I[1].

Results and Discussion

In order to discuss our results, reference has to be made:

(i) to the reaction scheme (1)–(12), which resumes the first part[1] of this investigation:

Excited-state

$$\mathrm{r} \xrightarrow{I_a} {}^1\mathrm{r} \qquad (1)$$

$$^1\mathrm{r} \overset{k_{ST}}{\rightsquigarrow} {}^3\mathrm{r} \qquad (2)$$

$$^{1,3}\mathrm{r} \xrightarrow{k_{F,P}} \mathrm{r} \qquad (3)$$

$$^{1,3}\mathrm{r} \overset{k_{C,TS}}{\rightsquigarrow} \mathrm{r} \qquad (4)$$

$$^{1,3}\mathrm{r} \xrightarrow{^{1,3}k_Q, Q} \mathrm{r} \qquad (5)$$

$$^{1,3}\mathrm{R} \underset{^{1,3}k_{21}}{\overset{^{1,3}k_{12}, H^+}{\rightleftharpoons}} {}^{1,3}\mathrm{RH} \qquad (6)$$

$$^{3}\mathrm{RH} \underset{^{3}k_{32'}\,\mathrm{SH}}{\overset{^{3}k_{23'}\,\mathrm{BS_4^-}}{\rightleftharpoons}} \underset{\textcircled{^{3}Y}}{^{3}(\mathrm{ROBS_3})} + \mathrm{SH} \qquad (7)$$

$$^{3}(\mathrm{ROBS_3}) \overset{k_3^*}{\rightsquigarrow} \mathrm{ROBS_3} \qquad (8)$$

Thermal

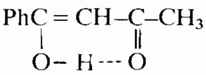
$$\mathrm{R} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{R_c} \qquad (9)$$

$$\mathrm{R_c} \underset{k_{21}}{\overset{k_{12'}\,\mathrm{H^+}}{\rightleftharpoons}} \mathrm{RH} \qquad (10)$$

$$\mathrm{RH} \underset{k_{32}}{\overset{k_{23'}\,\mathrm{BS_4^-}}{\rightleftharpoons}} \mathrm{ROBS_3} + \mathrm{SH} \qquad (11)$$

$$\underset{\textcircled{Y}}{\mathrm{ROBS_3}} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \underset{\textcircled{X}}{\mathrm{RO_2BS_2}} + \mathrm{SH}, \qquad (12)$$

where: 1,3: excited singlet or triplet; r: R or RH; R:



$$\mathrm{Ph}\underset{\substack{|\\ \mathrm{O-H}}}{\mathrm{C}}=\mathrm{CH}-\underset{\substack{\|\\ \cdots\mathrm{O}}}{\mathrm{C}}-\mathrm{CH_3}$$

; RH: $\mathrm{PhCO{-}CH_2C(OH)CH_3}$; $\mathrm{R_c}$: $\mathrm{PhCOCH_2COCH_3}$; ST and TS: $S_1 \rightsquigarrow T$ and $T_1 \rightsquigarrow S_o$ crossings; F,P: fluorescence or phosphorescence; C: internal conversion; Q: oxygen quencher; $\mathrm{BS_4^-}$: $\mathrm{B(OSO_3H)_4^-}$ or/and $\mathrm{B(OH)\ (OSO_3H)_3^-}$; SH: $\mathrm{H_2SO_4}$, and:

(ii) to the rate expression of chelate formation (13), and its integrated form (14)[1].

$$\frac{dX}{dt} = (M + N[A]_o)([R]_o - [X]) - W[X] - U, \qquad (13)$$

$$\ln \frac{[X]_e}{[X]_e - [X]} = k_{ir}^{obs} \cdot t = (\vec{k}_{ir}[A]_o + \overleftarrow{k}_{ir})t \qquad (14)$$

where

$[X]_e$: chelate concentration at equilibrium

$$k_{ir}^{obs} = [(M + N[A]_o)[R]_o - U]X_e^{-1} \qquad (15)$$

= observed rate constant upon continuous irradiation

$$\vec{k}_{ir}^* = N = \frac{k_{34}k_{23}k_1k_{-1}^{-1}k_{12}[H^+]}{(k_{32}' + k_{34})(k_{21} - \varphi^{**}\varepsilon_{RH}\ V^{-1}GI_o')}, (16)$$

$$\overleftarrow{k}_{ir}^* = M + W = \frac{k_{34}\ \Phi_{ST}\ \varepsilon_R V^{-1}GI_o'}{k_{32}' + k_{34}} + \frac{k_{32}'k_{43}'}{k_{32}' + k_{34}}, (16a)$$

$$\Phi_{ST} = k_{ST}[^1R]I_a^{-1} = k_{ST}/(^1k + {}^1k_{12}[H^+] - {}^1k_{21}[^1RH][^1R]^{-1}), \qquad (17)$$

$$^1k = k_F + k_C + {}^1k_Q[Q] + k_{ST} \quad \text{(referring to R)}, \qquad (18)$$

$$^3k = k_P + {}^3k_Q[Q] + k_{TS} \text{ (referring to R)}, \qquad (19)$$

$$\varphi^{**} = [(1 + \varphi'')/(1 + {}^1k_{21}{}^1k'^{-1})] - 1;$$

$$\varphi'' = \frac{^1k_{12}[H^+][^1R]}{I_a}, \qquad (20)$$

$$^1k' = k_F' + k_C' + {}^1k_Q'[Q] + k_{ST}' \quad \text{(referring to RH)}, \qquad (21)$$

$$^3k' = k_P' + {}^3k_Q'[Q] + k_{TS}' \quad \text{(referring to RH)}, \qquad (22)$$

I_o' = incident light intensity; V = volume of irradiated solution; G = a constant; A_o and R_o = initial concentrations of $\mathrm{BO_3H_3}$ and BZA; ε_R and ε_{RH} = molar absorptivities of R and RH; [X]: chelate concentration;

Effect of Proton Concentration

As can be seen from expressions (13), (14), (16), (16a), the overall rate constants $\vec{k}_{ir}$ and $\overleftarrow{k}_{ir}$ depend on thermal and photoexcited terms, the latter containing forward $^1k_{12}$ and reverse $^1k_{21}$ protolysis rate constants of the conjugated chelate form of the ligand (R) in the excited S_1 state (see (16a) and (17)).

In the case of $\overleftarrow{k}_{ir}$, this is simply the sum of the overall reverse ground-state chelate formation rate constant $\overleftarrow{k}_G$ and $\overleftarrow{k}_E$, including yield of the $^1R \rightsquigarrow {}^3R$ crossing:

$$\overleftarrow{k}_{ir} = \overleftarrow{k}_E + \overleftarrow{k}_G = \frac{k_{34}\ \Phi_{ST}\ \varepsilon_R V^{-1}GI_o'}{k_{32}[H^+] + k_{34}} + \frac{k_{43}k_{32}[H^+]^2}{k_{32}[H^+] + k_{34}}, \qquad (23)$$

Consequently, increasing acidity must result in a decrease of $\overleftarrow{k}_E$, but for validating possible quenching (see (17)) by the ^1R protolysis of the triplet populative process $^1R \rightsquigarrow {}^3R$ (which is the main source of production of the ^3RH photoreactive form[1]), the decrease of Φ_{ST} with increasing acidity must be significant.

Values of rate constants $k_{(12)}$ of chelate formation in 12% $\mathrm{H_2SO_4}$ (96%)/ether (V/V) solvent, upon ininterrupted irradiation of 4 × 10^{-5} Nhν/min intensity at 310 nm, are given in Table I together with $k_{(8)}$ (8% $\mathrm{H_2SO_4}$ (96%)/ether (V/V)) and the corresponding rate constants for ground-state complexation.

Comparison of k values (Table I), obtained from the k_{obs} *vs.* $[A]_o$ relations (see (14) and Figure 1),

TABLE I. Rate Constants for Dark and upon Continuous Irradiation for Chelate Formation (I_o' = 4 × 10^{-5} Nhν/min).

% $\mathrm{H_2SO_4}$/ EtOEt (V/V)	$\vec{k}_{ir}$ (M^{-1} min^{-1})	$\vec{k}_G$ (M^{-1} min^{-1})	$\overleftarrow{k}_{ir}$ (min^{-1})	$\overleftarrow{k}_G$ (min^{-1})
8	16.5	22.3	0.06	0.035
12	48.4	47.6	0.064	0.051

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* In the discussion that will follow on solvated proton effects, we shall assume that ring-opening in X and dissociation of Y proceed via rate-determining proton attack, so that $k_{32}' = k_{32}[H^+]$ and $k_{43}' = k_{43}[H^+]$.

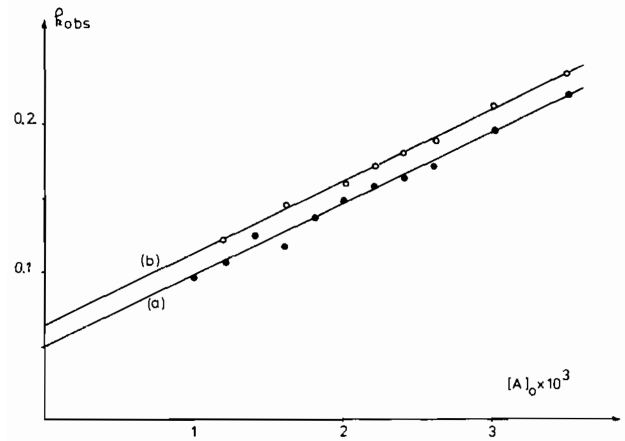

Figure 1. k_{obs} *vs.* initial boric acid concentration $[A]_o$ at 20° C ($[BZA]_o = 10^{-5}$); 12% H_2SO_4 (96%)/EtOEt (V/V); (a) dark complexation; (b) under continuous 310 nm irradiation of 4×10^{-5} Nhν/min intensity.

immediately shows the expected dependence of Φ_{ST} upon $[H^+]$. In fact, from expression (23) and values in Table I:

$$\Phi_{ST(12)}\ \varepsilon_{R(12)}\ (k_{32}[H^+]_{(8)} + k_{34})/\Phi_{ST(8)}\ \varepsilon_{R(8)}\ (k_{32}[H^+]_{(12)} + k_{34}) = (\overleftarrow{k}_{ir(12)} - \overleftarrow{k}_{G(12)}/(\overleftarrow{k}_{ir(8)} - \overleftarrow{k}_{G(8)}) = \overleftarrow{k}_{E(12)}/\overleftarrow{k}_{E(8)} = 0.52,\ \overleftarrow{k}_{G(8)}/\overleftarrow{k}_{G(12)} = (k_{32}[H^+]_{(12)} + k_{34})/(k_{32}[H^+]_{(8)} + k_{34}) = 0.686\,\alpha^2,\ (\alpha = [H^+]_{(12)}/[H^+]_{(8)}),$$

$$\frac{\Phi_{ST(12)}}{\Phi_{ST(8)}} = \frac{{}^1k + {}^1k_{12}[H^+]_{(8)} - {}^1k_{21}[{}^1RH][{}^1R]^{-1}}{{}^1k + {}^1k_{12}[H^+]_{(12)} - {}^1k_{21}[{}^1RH][{}^1R]^{-1}} = = 0.357\alpha^2\,\varepsilon_{R(8)}/\varepsilon_{R(12)}, \quad (24)$$

and since 1.5 is the highest possible value of α and plausibly $\varepsilon_{R(8)}/\varepsilon_{R(12)} \sim 1$, the diminution of Φ_{ST} with increasing acidity reflects, in agreement with the proposed mechanism, a more active competition of the ${}^1R \rightsquigarrow {}^3R$ crossing by the ${}^1R$ protolysis process.

Yet more significant may be the insensitivity, within experimental error, of the $\overrightarrow{k}_{(12)}$ to irradiation (see Fig. 1 and Table I), indicating that φ^{**} in 12% H_2SO_4/EtOEt becomes sufficiently low to make the $\varphi^{**}\varepsilon_{RH}V^{-1}GI_o'$ term negligible in expression (16). This is to be expected, since the bracketed term including φ'' in equation (20) increases with increasing proton concentration.

It is noteworthy that the above results bear kinetic evidence not only in favour of the proposed S_1 state interactions, but also in favour of our assumptions as to BZA's S_1 species populating the T_1 state with ligand photoreactive form. Thus, from spectral data it was concluded in part I of this work that ${}^1RH \rightsquigarrow {}^3RH \ll {}^1R \rightsquigarrow {}^3R$, and this is in agreement with the present quantitative deductions. In fact, if k_{ST}' (k_{ST}' for the ${}^1RH \rightsquigarrow {}^3RH$ crossing) was of comparable magnitude to k_{ST}, it can easily be shown that $\Phi_{ST} + \Phi_{ST}'$ replaces Φ_{ST} in expression (23), in which case the sum of yields ($\Phi_{ST} + \Phi_{ST}'$) had to raise or remain invariable, and not to decrease (see (24)) with increasing proton concentration.

External Heavy-atom Effect

Since it was shown that excited-state complexation can take place between boron species and benzoylacetone (BZA) in its lowest triplet state, the effect of the heavy-atom molecule Z (C_2H_5I) on the T ⟷ S processes of the R_c, R and RH forms of BZA was checked by emission spectroscopy and phosphorescence lifetime determinations. As expected, T ⟷ S transitions of all the above forms were markedly affected by Z.

Phosphorescence emissions of the diketo R_c form at 77 K, from clear SE (8% H_2SO_4 (96%)/ether (V/V)) and SE + Z glasses (Fig. 2, a and b), undoubtedly suggests a $k_{ST} > k_p > k_{TS}$ order of sensitivity to the external perturbation, with perhaps $k_p \gg k_{TS}$, since Z ($\varepsilon_{250} = 360$) in the concentration used absorbs considerably in the region of the R_c excitation (250 nm).

However, in the case of the conjugate chelate form R and the protonated one RH, the order is $k_{ST} > k_{TS} > k_p$. In fact, Fig. 2 shows that total emission at 77 K (Fig. 2, c' and e') of both R and RH, excited with 370 nm[1] light which is not at all absorbed by Z, considerably decreases with increasing Z concentration, while phosphorescence slightly diminishes (fig. 2, b').

Phosphorescence life-times of R_c and R were also found to be shorter in SE + Z matrices. According to expectation[2,3], $T_1 \rightarrow S_o$ decay curves of R_c (excited at 248 nm) and R (excited at 350 nm) were non-exponential when SE + Z glasses were used, but initial slopes of these curves were higher and the 36.7% decay times shorter, than in SE glasses (Table II).

Influence of Ligand T ⟷ S Enhancements on the Kinetics of the BZA–BO_3H_3 Interaction

Independently of the nature of the singlet states and the mixing routes[4–7] responsible of increasing T ⟷ S transition probabilities, from a kinetic point of view, in the presence of Z expressions (18), (19), (21) and (22) become:

$${}^1k_z = k_F + k_C + k_Q[Q] + k_{ST} + k_{STZ}[Z], \quad (25)$$

$${}^3k_z = k_p + {}^3k_Q'[Q] + k_{TS} + k_{TSZ}[Z] \quad (26)$$

$${}^1k_z' = k_F' + k_C' + {}^1k_Q'[Q] + k_{ST}' + k_{STZ}'[Z], \quad (27)$$

$${}^3k_z' = k_p' + {}^3k_Q'\,[Q] + k_{TS}' + k_{TSZ}'[Z]. \quad (28)$$

However, since spin-reversal process of the nonchelate boron intermediate can also be affected by Z:

$$\frac{d[{}^3Y]}{dt} = {}^3k_{23}[BS_4^-][{}^3RH] - ({}^3k_{32}' + k_3^* + k_{3Z}^*[Z])[{}^3Y], \quad (29)$$

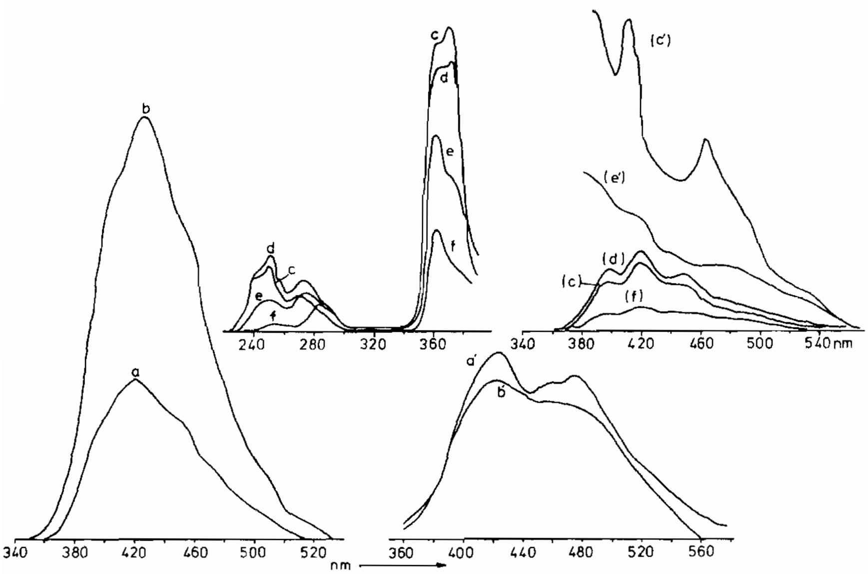

Figure 2. Phosphorescence (a, b, a', b') and total excitation–emission (c to f – (c') to (f)) spectra of BZA 5 × 10^{-3} in SE solvent at 77 K. a: BZA; b: BZA + 10^{-1} C_2H_5I (exc. 250 nm); a': BZA; b': BZA + 10^{-1} C_2H_5I (exc. 370 nm); (c'): BZA; (e'): BZA + 10^{-1} C_2H_5I (exc. 370 nm); (c): BZA; (d): BZA + 5 × 10^{-2} C_2H_5I; (f): BZA + 5 × 10^{-1} C_2H_5I (exc. 250 nm).

TABLE II. Times[a] (τ') of 36.7% Phosphorescence Decay of the Diketo (R_c) and the Conjugate Chelate (R) Forms of BZA in SE and SE + C_2H_5I Solvent.

	BZA: 2×10^{-2} (*M*)					
	Exc: 248 nm, Em: 419 nm (R_c)			Exc: 350 nm, Em: 480 nm (R)		
C_2H_5I(*M*)	0	10^{-1}		0	10^{-1}	
τ' (ms)	67	33		1200[b]	700	
	BZA: 5×10^{-2} (*M*)					
C_2H_5I(*M*)	0	2.5×10^{-2}	2.5×10^{-1}	0	2.5×10^{-2}	2.5×10^{-1}
τ' (ms)	64	45	36	1200[b]	720	610

[a] τ' of R_c and R (BZA: 2×10^{-2}) in SE + 10^{-1} highly purified CH_2Br_2 were 44 ms and 840 ms resp. [b] P. *vs.* t: exponential.

which gives (see part I), after introducing steady-state conditions for ^3R, ^3RH and ^3Y:

$$[^3Y] = (\Phi_{ST}{}^{Z} + \Phi_{ST}{}^{Z'})I_a - {}^3k_z[^3R] - {}^3k_z{}' [^3RH](k_3{}^* + k_{3Z}{}^*[Z])^{-1} \quad (30)$$

where:

$$\Phi_{ST}{}^{Z} = k_{ST} + k_{STZ}[Z]/({}^1k_Z + {}^1k_{12}[H^+] - {}^1k_{21} [^1RH][^1R]^{-1}) \quad (31)$$

$$\Phi_{ST}{}^{Z'} = k_{ST}{}' + k_{STZ}{}'[Z]/({}^1k_Z{}' + {}^1k_{21} - {}^1k_{12} [H^+][^1R][^1RH]^{-1}) \quad (32)$$

In part I of this work it could be shown that:

$$\Phi_{ST}(= k_{ST}[^1R]I_a{}^{-1}) \gg \Phi_{ST}{}' \; (= k_{ST}{}'[^1RH]I_a{}^{-1}),$$

but in the presence of the heavy-atom molecule Z, $\Phi_{ST}{}^{Z'}$ may not be negligible compared to $\Phi_{ST}{}^{Z}$ since, as was deduced above, the $S_{1(RH)} \rightsquigarrow T_{(RH)}$ crossing probability is considerably increased.

Proceeding now to the same development as in part I, the following rate expression for the chelate X formation is obtained:

$$\frac{d[X]}{dt} = (M' + N'[A]_o)(R_o - X) - W[X] - U' \quad (33)$$

where:

$$M' = k_{34}(\Phi_{ST}{}^{Z} + \Phi_{ST}{}^{Z'})\varepsilon_R V^{-1} G' I_o{}'/(k_{32}{}' + k_{34}), \quad (34)$$

$$N' = \frac{k_{34}k_{23}k_1k_{-1}{}^{-1}k_{12}[H^+]}{(k_{32}' + k_{34})(k_{21} - \varphi_Z{}^{**}\varepsilon_{RH}V^{-1}G'I_o')}, \quad (35)$$

$$\varphi_Z{}^{**} = [(1 + \varphi_Z'')/(1 + {}^1k_{21}{}^1k_z{}'^{-1})]-1, \quad (36)$$

$$\varphi_Z'' = {}^1k_{12}[H^+][{}^1R]_Z\, I_a{}^{-1} \quad (37)$$

with $[^1R]_z$ = photostationary concentration of ^1R,

$$W = k_{32}k_{43}'/(k_{32}' + k_{34}), \quad (38)$$

$$U' = ({}^3k_z[{}^3R] + {}^3k_z'[{}^3RH])/(k_{32}' + k_{34}), \quad (39)$$

V = volume of irradiated solution. G′ = a constant.

The observed rate constant of the X formation has now as expression:

$$k_{ir(Z)}{}^{obs} = [(M' + N'[A]_o)[R]_o - U'][X]_e{}^{-1} = \overrightarrow{k}_{ir(Z)}[A]_o + \overleftarrow{k}_{ir(Z)}, \quad (40)$$

with:

$$\overrightarrow{k}_{ir(Z)} = N' \quad (41)$$

$$\overleftarrow{k}_{ir(Z)} = M' + W'. \quad (42)$$

Tables III and IV give the observed rate constants $k_{(Z)}{}^{obs}$ and the values of $\overrightarrow{k}_z$ and $\overleftarrow{k}_z$ in the presence of 7.41 × 10^{-1} *M* C_2H_5I for dark complexation ($k_{G(Z)}$) and under uninterrupted 310 nm irradiation of various intensities ($k_{ir(Z)}$).

As in the case of irradiated solutions of BO_3H_3 + BZA in SE solvent, no photodecomposition could be

TABLE III. Observed ($k_{G(Z)}{}^{obs}$), Forward ($\overrightarrow{k}_{G(Z)}$) and Reverse ($\overleftarrow{k}_{G(Z)}$) Rate Constants for Dark Chelate Formation in the Presence of 0.741 *M* C_2H_5I in SE Solvent.

Absorption Spectrophotometry[a] $[BZA]_o$: 3 × 10^{-5} (*M*)			Fluorometry[b] $[BZA]_o$: 10^{-5} (*M*)		
$[A]_o \times 10^3$	$k_{G(Z)}{}^{obs}$		$[A]_o \times 10^3$	$k_{G(Z)}{}^{obs}$	
5	0.155	r[c]: 0.989	1	0.0765	r: 0.999
6	0.179	$\overrightarrow{k}_{G(Z)}$: 20.7 ± 0.49[d]	2	0.0938	$\overrightarrow{k}_{G(Z)}$: 18.7 ± 0.43
7	0.191	$\overleftarrow{k}_{G(Z)}$: 0.0517 ± 2.1 × 10^{-3}	3	0.1153	$\overleftarrow{k}_{G(Z)}$: 0.0538 ± 1 × 10^{-3}
8	0.220		4	0.1317	

[a] Monitoring chelate formation at 350 nm. [b] Monitoring chelate formation at 382 nm, with minimum excitation (341 nm) slit width. [c] r: linear regression coeff. of the $k_{G(Z)}{}^{obs}$ *vs.* $[A]_o$ relation. [d] $s = t\sigma/\sqrt{N}$; σ: standard error.

TABLE IV. Observed ($k_{ir(Z)}{}^{obs}$), Forward ($\overrightarrow{k}_{ir(Z)}$) and Reverse ($\overleftarrow{k}_{ir(Z)}$) Rate Constants of Chelate Formation upon Continuous Irradiation in the Presence of 0.71 *M* C_2H_5I in SE Solvent ($[BZA]_o$ = 10^{-5}).

I_o': 1.33 × 10^{-5} Nhν/min					2.04 × 10^{-5}				
$[A]_o$ × 10^3	$k_{ir(Z)}{}^{obs}$	r	$\overrightarrow{k}_{ir(Z)}$	$\overleftarrow{k}_{ir(Z)} \times 10^3$	$[A]_o$ × 10^3	$k_{ir(Z)}{}^{obs}$	r	$\overrightarrow{k}_{ir(Z)}$	$\overleftarrow{k}_{ir(Z)} \times 10^3$
1.5	0.0917				1	0.0775			
2	0.0945				1.5	0.0913			
2.5	0.1117	0.971	18.4	62	2.5	0.1116	0.993	20.3	59
3	0.1138		±0.88	±1.9	3.0	0.1180		±1.1	±1.7
3.5	0.1282								
	2.83 × 10^{-5}					4 × 10^{-5}			
1	0.0801				1.5	0.101			
1.5	0.0884				2	0.1077			
2	0.098	0.999	19.1	60	2.5	0.1152	0.995	17.2	74
3	0.1179		±0.39	±0.4	3.5	0.1351		±0.53	±1
	4.48 × 10^{-5}								
1	0.0831								
1.5	0.1047								
2	0.121								
2.5	0.1336	0.943	22.7	68					
3	0.1272		±1.3	±3.2					
3.5	0.1468								

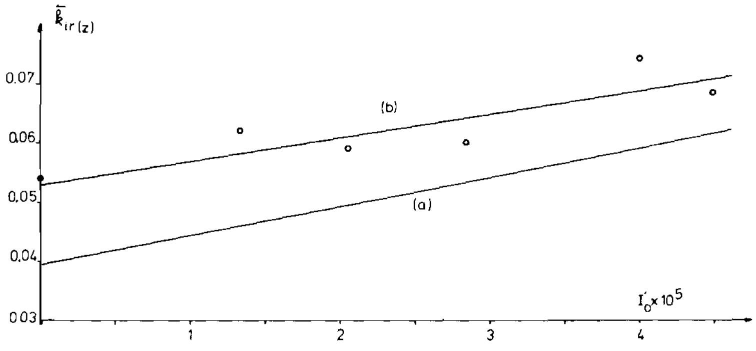

Figure 3. Reverse rate constant (continuous irradiation) *vs.* I_o'. (b) in the presence of 0.741 *M* C_2H_5I; •: value for dark complexation; (a) in the absence of C_2H_5I.

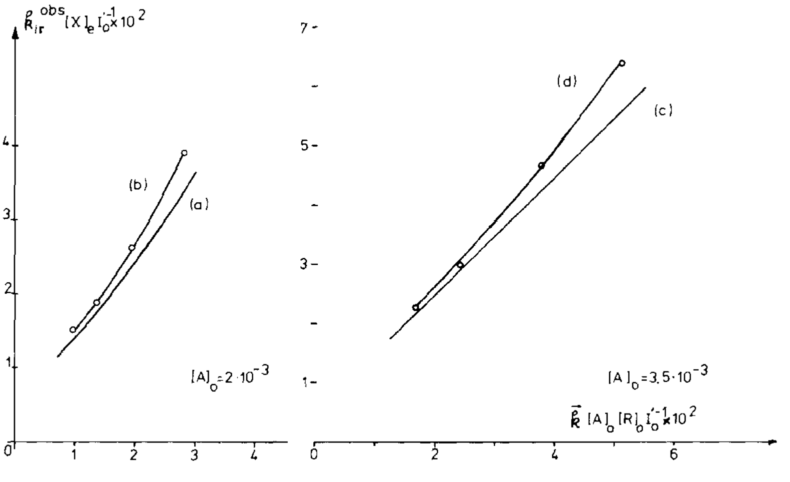

Figure 4. $k_{ir}^{obs}[X]_e\ I_o'^{-1}$ *vs.* $\bar{k}[A]_o[R]_o I_o'^{-1}$. (b) and (d) in the presence of 0.741 *M* C_2H_5I; (a) and (c) in the absence of C_2H_5I.

observed in the same solvent, containing the heavy-atom molecule.

Fig. 3, representing the $\bar{k}_{ir(Z)}$ *vs.* I_o' and $\bar{k}_{ir}$ *vs.* $I_o'^{1}$ variations shows an insensitivity of the $k_{ir(Z)}$ *vs.* I_o' slope to the external perturbation. From expression (42) this may appear quite surprising but, in fact, this insensitivity is only apparent.

As a matter of fact, the ratio $(\Phi_{ST}^{Z} + \Phi_{ST}^{Z'})/\Phi_{ST}$ (see figure 3a and b) has the value:

$$(\Phi_{ST}^{Z} + \Phi_{ST}^{Z'})/\Phi_{ST} = M'G/MG' = 0.8\ G/G' = 2.77^{*}, \quad (43)$$

since in the presence of 7.41 × 10^{-1} of Z (ε_z^{310} = 2.2) the intensity absorbed by R or RH is[1] (r: R or RH):

$$I_{a(r)} = I_o'V^{-1}G\varepsilon_rC_r = (1-\exp-[2.302\, l\sum_i\varepsilon_iC_i])/\varepsilon_rC_r/\sum_i\varepsilon_iC_i \simeq I_o'V^{-1}\varepsilon_rC_r/\sum_i\varepsilon_iC_i \simeq I_o'V^{-1}\varepsilon_rC_r/(\varepsilon_R[R]_o + \varepsilon_Z[Z]) \simeq I_o'V^{-1}G'\varepsilon_rC_r, \quad (44)$$

giving G' = 0.56 and as G = 1.94[1], G/G' = 3.46.

The value of the triplet quantum yield ratio (43) undoubtedly suggests an increased $S_1 \rightsquigarrow T$ efficiency mediated by Z, but it is difficult to determine which (^1R or ^1RH) is the most actively depleted form by $S_1 \rightsquigarrow T$ crossing.

Another point of interest relative to the external perturbation is the independency of $\bar{k}_{ir(Z)}$ on I_o' (Table II). This can be explained in terms of increased probability of ^1R and ^1RH depletions induced by Z. In fact, φ'', depending directly on the photostationary concentration $[^1R]$, becomes lower in the presence of

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* This calculated value (see 16(a) and (42)) is to be considered as a lower limit of the yield ratio. In fact, while the overall forward ground-state rate constant does not change significantly when passing from SE solvent ($\bar{k}_G$ = 22.3) to SE + Z ($\bar{k}_{G(Z)}$ = 19.7), the reverse one, $\bar{k}_G$, increases (see intersections at the origin, figure 3 and ref. 1). If, then, in the presence of Z both k_{43}' and k_{32}' have higher values $(\Phi_{ST}^{Z} + \Phi_{ST}^{Z'})/\Phi_{ST} > 2.77$.

Z, while ${}^1k'$ increases by the additional pseudo-monomolecular term ${}^1k_{STZ}'[Z]$. It is, therefore, quite possible that φ_Z^{**} has a very low value (see (36)) in the presence of the heavy-atom perturber, thus making the $\varphi_Z^{**}\,\varepsilon_{RH}V^{-1}G'I_o'$ term negligible in expression (35).

Turning now to BZA lowest triplet-state processes in the presence of Z, one would expect a more active quenching of the boron species complexation by ^{3}RH (see (7)), due to enhanced T_1 degradations of ^{3}R and ^{3}RH. In order to check this point, expression (40), containing kinetic terms for ligand T_1 degradations, can be used in the following form (see discussion on the size of φ_Z^{**}):

$$k_{ir(Z)}{}^{obs}[X]_eI_o'^{-1} = M'[R]_o + \vec{k}[A]_o[R]_o \\ I_o'^{-1} - ({}^3k_z[{}^3R] + {}^3k_z'[{}^3RH])I_o'^{-1}/(k_{32}' + k_{34})$$

It is noteworthy that an increase of $[A]_o$ up to 3.5×10^{-3} *M* is insufficient to linearise the $k_{ir(Z)}{}^{obs}[X]_eI_o^{-1}$ *vs.* $\vec{k}[A]_o[R]_oI_o'^{-1}$ function (Figure 4d). With 3.5×10^{-3} *M* total concentration $[A]_o$ of boric acid and in the absence of Z, linearisation of the above function, by nearly complete quenching of ligand $T_1 \rightsquigarrow S_o$ transitions, occurs however (see Figure 4c and ref. 1), so that this behaviour provides further kinetic evidence in favour of boron species complexation by ^{3}BZA.

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